THERMODYNAMIC ANALYSIS OF CaO - SiO2 - Al2O3 - MgO SLAG SYSTEM

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Abstract

The paper deals with the possibility of thermodynamic analysis of CaO - SiO2 - Al2O3 - MgO slag system for optimizing of steel desulphurization in a ladle. From the point of view of reducing the sulphur content in steel, the chemical composition of the slag plays a crucial role which affects a critical thermodynamic parameter of the slag, such as the liquidus temperature of the slag, the amount of solid phases in slag at range of refining temperatures, respectively the effective viscosity of slag and CaO saturation in slag. The critical parameters were analyzed in dependence on the content of MgO in slag. The analysis was performed in FactSage 7.2 software. A quaternary graphs of the slag system CaO - SiO2 - Al2O3 - MgO were created with a constant MgO content of 0 wt.%, 5 wt.%, 10 wt.% and 15 wt.%. The results of thermodynamic calculations confirm that the content of MgO among 5% and 10% will have a positive effect on expanding the area of the lowest liquidus temperature and therefore better viscosity of slag. On the other hand, the content of MgO above 8 % led to higher content of solid phases which affected negatively the viscosity.

Keywords: FactSage, properties of ladle furnace slag, furnace ladle slag, basicity of ladle furnace slag, temperature of liquid slag

1. INTRODUCTION

Improving the competitiveness of steel companies is associated with sustainable, satisfactory steel production. Ladle metallurgy is the last place where you can further adjust the chemical composition of steel, partially remove inclusions from steel and reduce unwanted elements in steel, such as sulphur. Under operating conditions, it is often very difficult to perform a series of targeted experiments to verify the effectiveness of the selected metallurgical process to reduce sulphur content, so simulation software is used to help optimize production processes [1-4].

One of the helpful software that can be used in evaluating the course of metallurgical processes is FactSage. FactSage is a thermodynamic/thermochemical software which is based on thermodynamic calculations of energy functions from empirically obtained values of thermo-physical properties of materials (heat capacities, enthalpies, phase transformation temperatures, etc.), both steels and slag, determines eg. phase or chemical transformations during metallurgical processes [5-7].

One of the main parameters that affects desulphurization is the saturation of CaO in the slag. The lime saturation index is an important parameter that is determined as the ratio of the actual CaO content to the CaO content of the saturated slag lime. The authors of the article [8] claim that saturated calcium slags have the highest desulphurization effectivity. Insufficient lime saturation in the ladle slag leads to a reduction in the desulphurization effect. Higher MgO content in the slag affects the desulphurization processes. The authors

found that increasing the content of MgO in the slag leads to saturation of the MgO in the slag, resulting the extention of life of the refractory lining, but on the contrary deteriorating the desulphurization reaction rate steel. Therefore, it is important to find the optimal content of MgO in the slag, so that the MgO in the slag is saturated and positively affects the reaction rate of desulphurization. Great influence on the reduction of sulphur content in the steel has a significant influence of the solids and liquid phase. Effective viscosity means a lower solids content (lower viscosity) and ensures faster solubility of CaO in the slag. To keep the liquid phase of the slag, it is important that the CaO is saturated [8-11].

The main goal of the paper is to analyze the critical parameters that affect metallurgical processes during steel desulphurization. The main parameters that affect desulphurization are: CaO saturation in ladle slag, dependence of slag liquidus temperature on MgO content in slag, slag viscosity and MgO content on the fraction of the excluded phase.

2.   CHARACTERISTICS OF LADLE SLAG CaO - SiO_2 - Al_2O_3 - MgO

The data set used for the experimental study itself represents data with the appropriate chemical composition of the slags of 66 specific melts. Slags of steel grades with a similar chemical composition were selected. In all cases, it was aluminum-tempered steel. Tapping from the primary steelmaking, in this case the oxygen converter, was followed by out-of-furnace refining of the steel. Samples for determining the chemical composition of the slag were taken at the end of the processing of the steel in a ladle furnace. Ranges of chemical composition of ladle slags are given in **Table 1.**

Table 1 Ranges of chemical composition of the examined ladle slag

Chemical composition of ladle slag (wt.%)										
Fe_{total}	MnO	SiO_2	Al_2O_3	CaO	MgO	S	P_2O_5	Cr_2O_3	TiO_2	CaF_2
0.2 – 0.8	0.04 – 0.60	8 - 21	19 - 31	40 - 60	7 - 20	0.4 - 1	0.01 – 0.05	0 – 0.2	0.20 – 0.30	0 - 2

As it is evident from **Table 1** that CaO is present in the largest amount of the main oxides. The high occurrence of CaO in the slag indicates the slag regime, which is designed for desulphurization of steel. We know from theory that for the desulphurization of steel it is necessary to reduce the FeO content in the slag. However, experience shows that not only FeO in slag has an effect on the desulphurization of steel, but the content of MnO and MgO in slag also play an important role during metallurgical processes. 66 combinations of the chemical composition of ladle slags were subsequently used to calculate and compile quaternary diagrams of the properties of ladle slags in SW FactSage.

3.   COMPILATION OF QUATERNARY DIAGRAMS OF LADLES SLAGS AL2O3-SIO2-CAO-MGO IN SW FACTSAGE AND CALCULATION OF SLAG PROPERTIES

Quaternary diagrams were compiled for the slag system CaO - SiO2 - Al2O3 - MgO with a constant MgO content of 0 wt.%, 5 wt.%, 10 wt.% and 15 wt.%. The aim of the calculations was to determine the extent to which MgO affects the resulting properties of the slag. Practice shows that as the MgO content in the slag increases, the area of thermal liquidity of the slag, the amount of solid phase precipitated in the slag at steel processing temperatures and the saturation of the CaO slag also change dramatically.

3.1.   Determination of slag liquidus temperature

An important parameter for slag optimization is knowledge of its liquidus temperature. The liquidus temperature affects the rate and kinetics of the chemical reaction between the slag and the metal [12,13,18]. The liquidus temperature of ladle slags was determined for the chemical composition with a MgO content in the range of 0 to 15% by weight and at processing temperatures in the range from 1,450 to 1,650 °C. A comparison of

quaternary diagrams of slags with a constant MgO content of 0, 5, 10 and 15 wt.% is shown in **Figure 1**. The colors of the slag liquidus temperature scale to the right of the diagram correspond to the colors of the isotherms in the diagram. The isotherms in the diagram then define the area of the slag melting temperature area for individual ratios of the contents of the main components of ladle slag. The area defined in the diagram by the pink curve is therefore considered to be the place with the lowest liquidus temperature of 1,450 °C. In the red area, the liquidus temperatures reach 1,650 °C. During the desulphurization of steel in secondary metallurgy, metallurgical reactions take place in the diagram marked with an orange oval area. The diagram also intersects lines marking areas with different slag basicity.

a) 0% MgO

b) 5% MgO
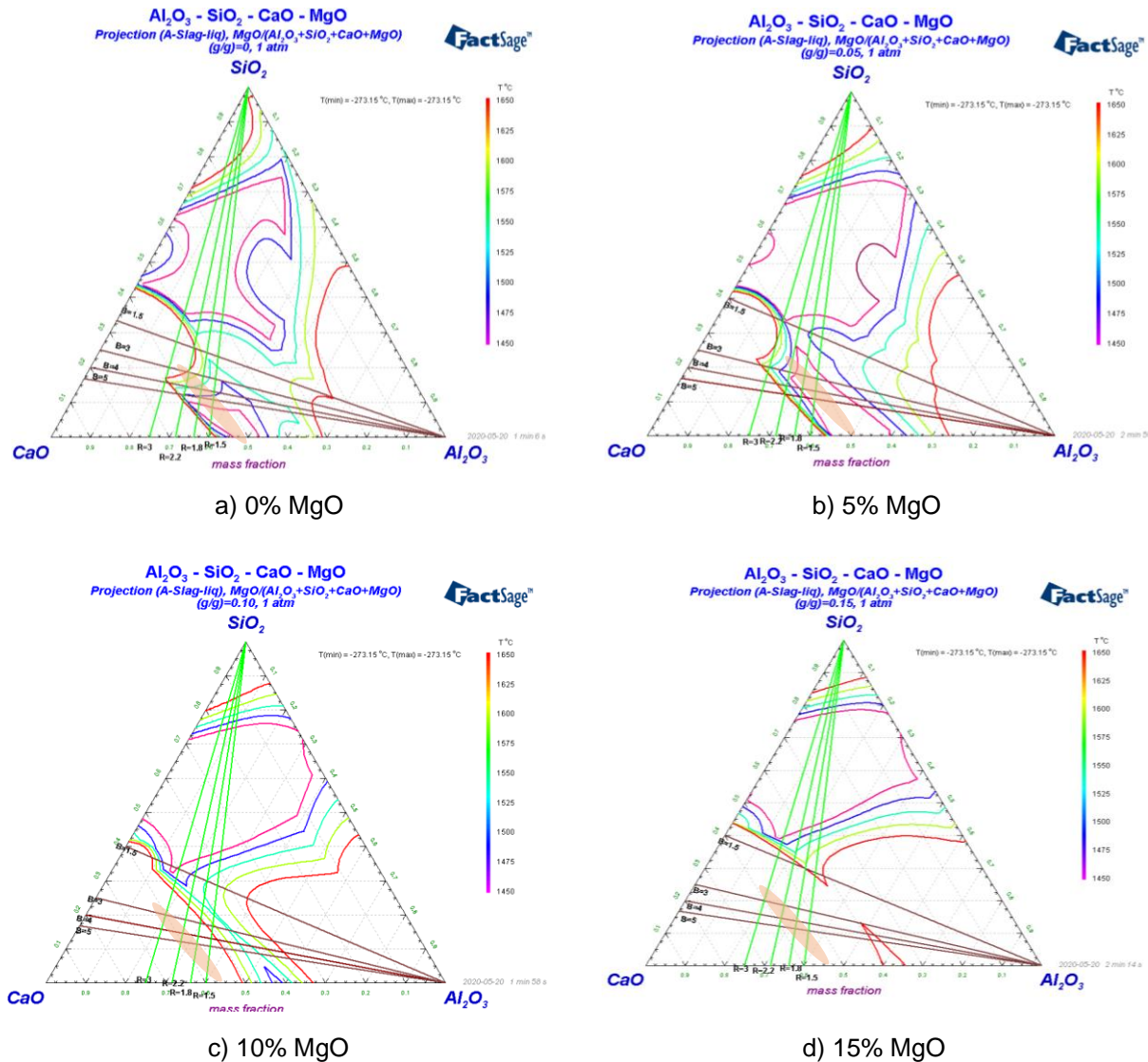
c) 10% MgO

d) 15% MgO

Figure 1 Comparison of quaternary diagrams of slag systems with a) 0% MgO, b) 5% MgO, c) 10% MgO d) 15% MgO and their liquidus temperatures

As can be seen from **Figure 1** for 0 wt.% MgO in the slag, all liquidus temperature ranges (isolines) are in the orange range, in the isolines have a narrow liquidus temperature range. When the MgO content in the slag is increased to 5%, the pink temperature range expands. Increasing the MgO to 10% results in the orange region suddenly reaching the red isothermal region (liquidus temperature 1,650 °C), which negatively affects the kinetics of the desulphurization process by increasing the viscosity. In addition, only one pink isothermal region is shown compared to the diagram with lower MgO contents in the slag. Furthermore, it is evident that when

the MgO content in the slag is increased to 15%, there are not very positive effects during the desulphurization of the steel due to the increase in the liquidus temperature. Therefore, the optimal MgO content in the slag, in the range of 5 to 10 wt.% MgO, was determined using FactSage software. As a result, it can be stated that increasing the amount of MgO in the slag to 10% will expand the area of liquid slag. By adding MgO above 10%, on the other hand, the liquid temperature of the slag increases and thus its viscosity deteriorates and the kinetics of the processes at the slag-metal interface are slowed down.

3.2. Determination of slag viscosity

The viscosity was evaluated depending on the MgO content, the melting point of the slag and the working temperature of the slag during steel processing in the temperature range 1,550 – 1,600 °C (based on articles [14-16]). The dynamic viscosity, depending on the temperature and chemical composition of the slag, ranged from 0.018 to 0.194 Pa s. Low viscosity values of 0.018 Pa s were achieved at high slag temperatures (above 1,650 °C) and zero MgO content. As the MgO content increased to 8%, the slag liquidus temperature range changed positively, which decreased to the processing temperature range (i.e., between 1,550 to 1,600 ° C), and a lower viscosity value of about 0.6-0.8 Pa s was achieved. However, higher MgO contents above 8% led to the exclusion of solid phases, as will be discussed below, which led to an increase in the dynamic viscosity of the slag.

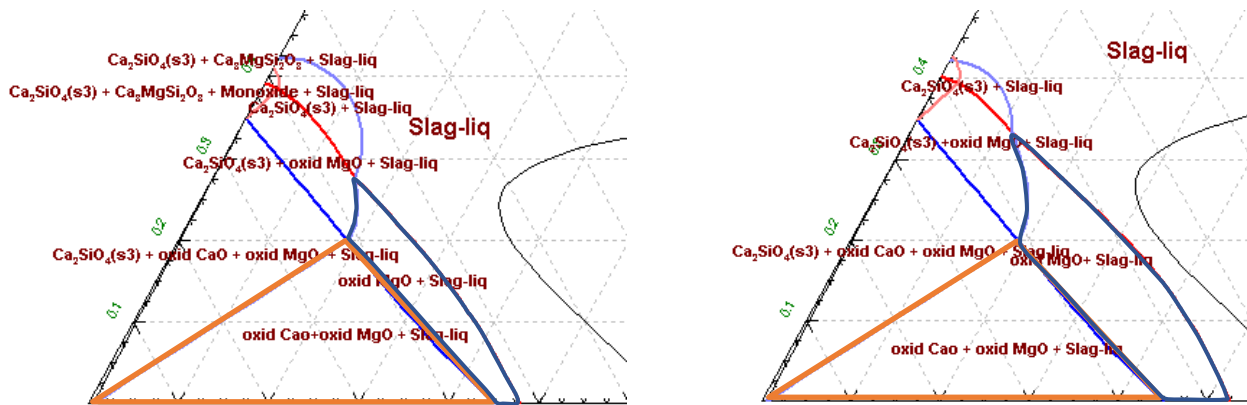### 3.3. Influence of MgO content on the fraction of the excluded phase

As mentioned above, the precipitation of the solid phase in the slag negatively affects the viscosity of the slag. Based on articles [13,17] we know, if the slag exceeds 40% of the solid phase, a highly viscous mass changes from the slag. **Figure 2** shows the proportions of precipitated phases which were evaluated at a constant temperature of 1,575 ° C for different contents of MgO (0, 5, 8, 10%). The size of the CaO secretion area, which is important for the evaluation of CaO saturation in slag, was evaluated in the diagrams. The site of primary CaO formation was considered to be the site where CaO saturation in the slag occurs. Slag-liq is an area with liquid slag. By adding 5% MgO to the slag, the area where CaO oxide is formed narrows and at the same time the area of liquid slag expands. When the MgO content is increased to 8%, the CaO area expands again, but at the same time an area with MgO excretion is already beginning to appear. By further increasing the MgO content above 10%, the area of liquid slag is already beginning to narrow and the area of excreted MgO is expanding.
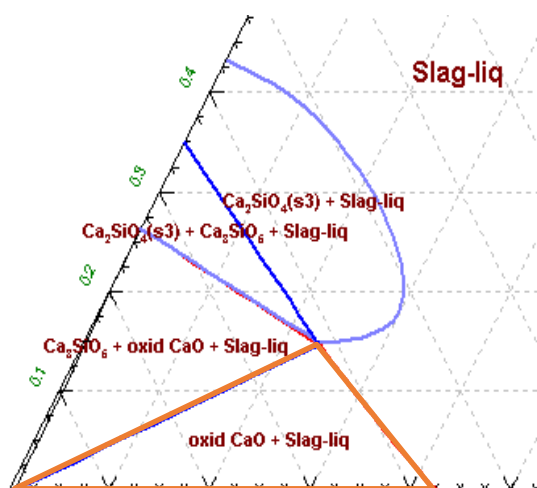
Lower left section of the ternary diagram C-S-A at a temperature of 1,575 ° C
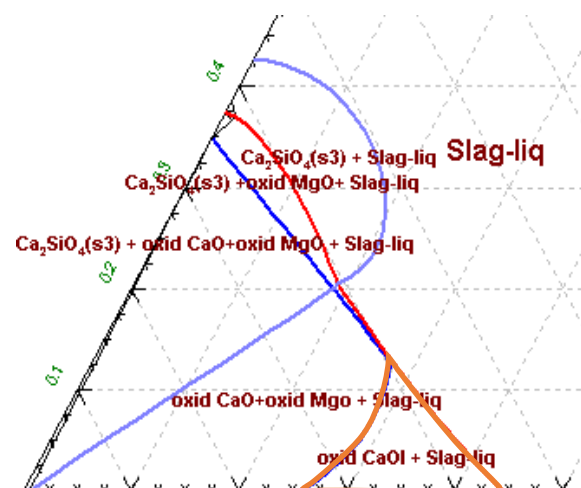
Lower left section of the quaternary diagram C-S-A-5M at 1,575 ° C

Lower left section of the quaternary diagram C-S-A-8M at 1,575 ° C

Lower left section of the quaternary diagram C-S-A-10M at 1,575 ° C

Figure 2 Influence of MgO content on phase formation

The MgO content positively influences the slag up to 5 wt.% A to form CaO oxide in the slag and expand the Slag-liq area. An increase in MgO to more than 8% and the formation of MgO oxide and a mixture of CaO and MgO in the orange region have a negative effect.

4.   CONCLUSION

The article presented the use of thermodynamic software FactSage to find the optimal chemical composition of CaO - SiO_2 - Al_2O_3 - MgO slag in the out-of-furnace desulphurization of steel in a ladle furnace. In practical conditions, the desulphurization efficiency is conditioned by the minimum content of easily reducible oxides (which mainly include FeO, MnO, P_2O_5 and Cr_2O_3), the maximum thermodynamic activity of CaO in the slag (CaO saturation), basicity, processing temperature and slag liquidus temperature and viscosity.

Based on the calculated and constructed quaternary diagrams of the slag system with a variable MgO content from 0 to 15%, the following conclusions were defined:

- The liquidus temperature of ladle slag depends on the MgO content. At 0% MgO in the slag, the area with the lowest slag liquidus temperature around 1,450 °C is relatively narrow. Increasing the MgO content between 5 and 10% will have a positive effect on expanding the area with the lowest liquidus temperature. If the MgO content is increased to 10% or more, the liquid slag area will narrow.
- Dynamic viscosity calculations confirmed that the viscosity is affected by the temperature and chemical composition of the slag. As the viscosity of the slag increases, the effective desulphurization of the steel decreases.
- Therefore, in order to achieve effective desulphurization, it is recommended to keep the MgO content in the ladle slag in the range of about 8% (between 5 and 10 wt.% MgO).

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